Canadian Sediment Quality Guidelines for the Protection of Aquatic Life

ZINC

Zinc (Zn) is an essential trace element that can be toxic to aquatic biota at elevated concentrations. Zinc enters aquatic systems through aerial deposition or surface runoff. The strong affinity of zinc for aquatic particles, particularly iron and manganese oxides, and organic matter results in its deposition in bed sediments in association with these materials (Campbell and Tessier 1996). A wide variety of organisms live in contact with the sediments of aquatic systems. Sediments therefore act as an important route of exposure to Zn for aquatic organisms. Canadian interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for Zn can be used to evaluate the degree to which adverse biological effects are likely to occur as a result of exposure to Zn in sediments.

Canadian ISQGs and PELs for Zn were developed using a modification of the National Status and Trends Program approach as described in CCME (1995) (Table 1). The ISQGs and PELs refer to total concentrations of Zn in surficial sediments (i.e., 5 cm), as quantified by digestion with a strong acid (e.g., aqua regia, nitric acid, or hydrochloric acid), followed with determination by a standard analytical protocol.

The majority of the data used to derive ISQGs and PELs for Zn are from studies on field-collected sediments that measured concentrations of Zn, along with concentrations of other chemicals, and associated biological effects as compiled in the Biological Effects Database for Sediments (BEDS) (Environment Canada 1998). The Zn data sets for freshwater and marine sediments are large, with the freshwater data set containing 88 effect entries and 369 no-effect entries and the marine data set containing 96 effect entries and 315 no-effect entries (Figures 1 and 2). The BEDS represents a wide range of concentrations of Zn, types of sediment, and mixtures of chemicals. Evaluation of the percentage of effect entries for Zn that are below the ISQGs, between the ISQGs and the PELs, and above the PELs for Zn (Figures 1 and 2) indicates that these values define three ranges of chemical concentrations: those that are rarely, occasionally, and frequently associated with adverse biological effects, respectively (Environment Canada 1998).

Toxicity

Adverse biological effects for Zn in the BEDS include decreased benthic invertebrate diversity and abundance, increased mortality, and behavioural changes (Environment Canada 1998, Appendixes IIa and IIb). Adverse effects were observed in a variety of freshwater and marine taxa, including Gastropoda, Amphipoda, Chironomidae, Echinodermata, and Annelida. For example, species richness of Ephemeroptera, Plecoptera, and Tricoptera was low in the Bay of Quinte (Lake Ontario) at locations where the mean concentration of Zn in sediments was 293 $mg \cdot kg^{-1}$, which is more than twice the freshwater ISQG. By comparison, higher species richness was observed at sites with a mean concentration of 119 $mg \cdot kg^{-1}$, which is below the freshwater ISQG (Jaagumagi 1988). Similarly, in the Curtis Creek estuary (Baltimore, Maryland), mortality of *Hyalella azteca*, an amphipod, was significantly increased at a mean concentration of 348 $mg \cdot kg^{-1}$, which is above the marine PEL, while no effect was observed at a mean concentration of 78.4 $mg \cdot kg^{-1}$, which is below the marine ISQG (McGee et al. 1993).

Spiked-sediment toxicity tests for Zn report the onset of toxicity to benthic organisms at higher concentrations than those observed in field studies. This is likely a result of the shorter exposure times of these laboratory studies and exposure to Zn only as opposed to chemical mixtures containing Zn (Environment Canada 1998). For example, the 28-d LC_{25} calculated for a freshwater amphipod, *Hyalella azteca*, was 3531 $mg \cdot kg^{-1}$, which is approximately 10 times higher than the freshwater PEL (Borgmann and Norwood 1997).

Table 1. Interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for zinc ($mg \cdot kg^{-1}$ dw).

	Freshwater	Marine/estuarine
ISQG	123	124
PEL	315	271

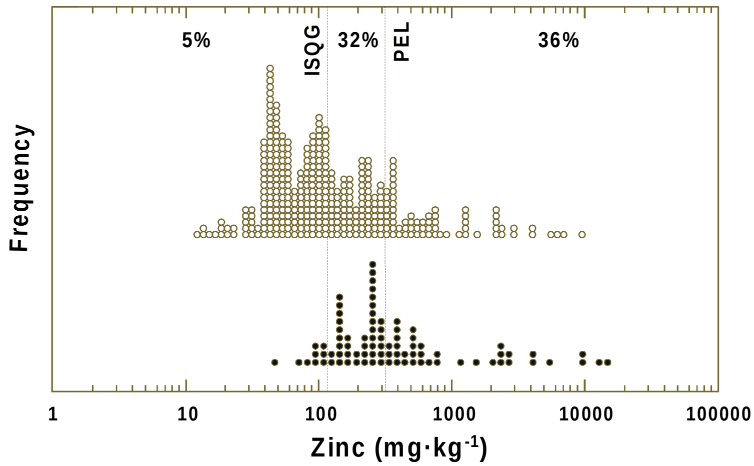

Figure 1. Distribution of Zn concentrations in freshwater sediments that are associated with adverse biological effects (●) and no adverse biological effects (○). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.

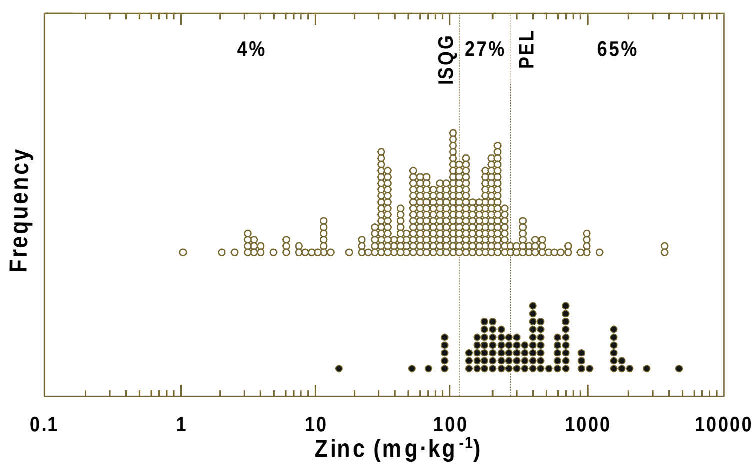

Figure 2. Distribution of Zn concentrations in marine and estuarine sediments that are associated with adverse biological effects (●) and no adverse biological effects (○). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.

Similarly, Oakden et al. (1984) observed >50% mortality in amphipods (*Rhepoxynius* spp.) after a 72-h exposure to concentrations of Zn that were approximately twice the marine PEL. In sublethal spiked-sediment toxicity tests, marine amphipods (*Rhepoxynius* spp.) showed a statistically significant preference for clean sediments over sediments spiked with 51 $mg \cdot kg^{-1}$ Zn, which is below the marine ISQG (Oakden et al. 1984).

The toxicity of Zn in sediments can be mitigated by various sediment fractions that play a protective role (Environment Canada 1998). For example, organic matter and sulphides have been found to reduce the toxicity of sediment-associated Zn (Sibley et al. 1996).

Results of both freshwater and marine spiked-sediment toxicity tests indicate that concentrations of Zn that are associated with adverse effects are consistently above the ISQGs, confirming that these guidelines represent concentrations below which adverse biological effects will rarely occur. Further, these studies provide additional evidence that toxic levels of Zn in sediments are similar to or greater than the PELs, confirming that adverse effects are more likely to be observed when concentrations of Zn exceed the PELs. The ISQGs and PELs for Zn are therefore expected to be valuable tools for assessing the ecotoxicological relevance of concentrations of Zn in sediments.

Concentrations

Concentrations of Zn in marine and freshwater sediments vary substantially across Canada (Environment Canada 1998). In the National Geochemical Reconnaissance (NGR) program database by the Geological Survey of Canada (GSC) (Friske and Hornbrook 1991), the mean background concentrations of Zn in Canadian lake and stream sediments are 104 $mg \cdot kg^{-1}$ and 107 $mg \cdot kg^{-1}$, respectively (P.W.B. Friske 1996, GSC, Ottawa, pers. com.). When compared with the background concentrations in the combined lake and stream NGR database (n = 154 889), the freshwater ISQG and PEL for Zn fall at percentiles 77.8 and 97.8, respectively, (R.G. Garrett 1997, GSC, Ottawa, pers. com.), demonstrating that background concentrations of Zn across most of Canada are lower than the ISQG of 123 $mg \cdot kg^{-1}$. In marine systems, mean background concentrations of Zn, estimated from deep layers of sediment cores (>10 cm) from a variety of published sources, ranged from 13.1 to 1170 $mg \cdot kg^{-1}$ (i.e., below the marine ISQG to well above the PEL) (Environment Canada 1998).

Concentrations of Zn in surficial sediments located close to point sources of contamination frequently exceed estimates of background concentrations (Environment Canada 1998). For example, mean concentrations as high as 7366 $mg \cdot kg^{-1}$ have been measured in sediments from freshwater lakes near mining and smelting operations and as high as 5100 $mg \cdot kg^{-1}$ in marine harbours receiving various industrial inputs (Environment Canada 1998).

Additional Considerations

Regardless of the origin of Zn in sediments, aquatic organisms may be adversely affected by exposure to elevated levels. As is evident in Figures 1 and 2, the occurrence of adverse biological effects cannot be precisely predicted from concentration data alone, particularly in the concentration ranges between the ISQGs and PELs. The likelihood of adverse biological effects occurring in response to Zn exposure at a particular site depends on the sensitivity of individual species and endpoints examined, as well as a variety of physicochemical (e.g., pH and redox potential), geochemical (e.g., particle size, organic matter content, and metal oxide and sulphide contents), and biological (e.g., feeding behaviour and uptake rates) factors that affect the bioavailability of Zn (Environment Canada 1998).

Benthic organisms are exposed to both particulate and dissolved forms of Zn in interstitial and overlying waters, as well as to sediment-bound Zn through surface contact and sediment ingestion. Dissolved forms of Zn are believed to be the most readily bioavailable (Campbell and Tessier 1996). Zinc associated with sediment fractions that exhibit cation-exchange capacity or that are easily reduced is generally more bioavailable than that associated with other fractions (Environment Canada 1998). Furthermore, changes in ambient environmental conditions (e.g., sediment turbation, decrease in pH, and increase in redox potential) can increase the bioavailability of Zn associated with inorganic solid phases, oxides of iron and manganese, and organic matter. In contrast, Zn that is bound within the crystalline lattices of clay and some other minerals that are associated with acid-extractable or residual sediment fractions is generally considered to be the least bioavailable. Once Zn is ingested, its availability depends on various factors, including enzyme activity and gut pH (Environment Canada 1998).

Models have been proposed to predict metal uptake (and hence toxicity) in aquatic organisms from bed sediments. Tessier et al. (1993) propose that bioavailability, as measured by accumulation of Zn in the organism, can be predicted by calculating the dissolved metal concentration in the interstitial and overlying water of oxic sediments. This prediction considers the quantity of Zn loosely associated with major sinks, such as organic matter and metal oxides, and the physicochemical factors that influence the distribution of Zn between the dissolved phase and the aforementioned phases. Dissolved metal concentrations in interstitial and overlying waters calculated using this model have been demonstrated to correlate well with metal levels in the soft tissues of benthic invertebrates (Couillard et al. 1993; Tessier et al. 1993, Hare and Tessier 1996). Another model that has been proposed considers the role of acid volatile sulphide (AVS) in modifying the bioavailability of two simultaneously extractable metals (SEM), cadmium and nickel, in anoxic sediments (Di Toro et al. 1992). This model is applicable to Zn and other metals that form sulphides. Acid volatile sulphide refers to the fraction of the sediment that contains a reactive pool of solid-phase sulphide that is available to bind divalent metals and thus render them unavailable for uptake by aquatic biota. The model predicts that when the molar ratio of SEM to AVS in sediments is <1, metals will not be bioavailable due to complexation with available sulphide. When the ratio is >1, the bioavailability of SEM is predicted to be high. However, when the ratio is >1, the model has several limitations, as it does not take into account the importance of other binding phases that will also limit the bioavailability of a metal (Hare et al. 1994; Environment Canada 1998). In addition to geochemical factors, further research should be directed at determining other factors that modify the bioavailability of Zn (e.g., physical, chemical, and biological factors). This information should be considered, along with the recommended ISQGs and PELs, in site-specific assessments of Zn in sediments.

Currently, the degree to which Zn will be bioavailable at particular sites cannot be predicted conclusively from the physicochemical characteristics of the sediment or the attributes of endemic organisms (Environment Canada 1998). Nonetheless, the incidence of adverse biological effects associated with exposure to Zn increases as concentrations of Zn increase in a range of sediment types (Figures 1 and 2). Therefore, the recommended Canadian ISQGs and PELs for Zn will be useful in assessing the ecotoxicological significance of Zn in sediments.

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